REMARKS

Status of Claims

Claims 1-2, 4-6, 9, 10 and 12-15 are pending in the instant application. Claims 1-2, 4-6, 9, 10 and 12-15 stand rejected. Favorable reconsideration is respectfully requested in light of the following remarks.

Rejection of Claims 1-2, 6-7 and 12-14 under 35 U.S.C. 103(a)

Claims 1-2, 6, 9-10 and 12-15 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Dana et al. (U.S. 5,908,689) in view of Das et al. (U.S. 4,637,956).

The Examiner states in the "Response to Arguments" section of the Official Action, that neither Dana et al. nor Das et al. disclose the weight of the sizing composition, however, the weight of the sizing composition can be optimized in order to improve the bonding strength between the fibers and the resin. The Examiner further states that the optimization of the sizing composition is not without motivation.

Applicants respectfully traverse this rejection. Applicants respectfully submit that it is not routine in the art to apply a significant amount of sizing on reinforcing fibers. "Sizings are designed to protect the reinforcement during processing and must coat the surface uniformly", ASM Handbook – Vol. 21 Composites (copy attached).

Clearly, Dana et al. and Das et al. teach away from applying a significant amount of sizing on glass fibers. It is well-known in the art to apply sizings in small quantities as both Dana et al., Das et al. and numerous other patents teach. Further, Applicants have included excerpts from two composites trade organizations' web pages "Composites World" and "Composites-one.com" teaching the standard practice of applying sizing in an amount between 0.25 and 6 percent of the total fiber weight. Applicants also have including a citation from the "ASM Handbook – Vol. 21 Composites" stating, "Sizings are usually applied at a level of 1.0% or less….."

Accordingly, one of ordinary skill in the art would not be motivated to apply a chemical treatment on fibers in an amount of between 5% to 30% by weight as Applicants claim.

It is respectfully submitted that the Office Action does not meet the criteria for establishing a *prima facie* case of obviousness. To establish a *prima facie* case of obviousness, three criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the applied reference must teach or suggest all the claim limitations. The mere fact that references can be combined or modified does not render the resultant combination obvious unless the prior art also suggests the desirability of the combination. Further, the fact that the claimed invention is within the capabilities of one of ordinary skill in the art is not sufficient by itself to establish a *prima facie* case of obviousness without some objective reason to combine the teachings of the references. See MPEP §2143.

Nowhere do Dana et al. teach or suggest reinforcing fibers having an applied chemical treatment on the fibers from 5% to 30% by weight, as Applicants claim. Dana et al. specifically teach that the "weight of the sizing composition on the fibers….was about 2.15 weight percent" (col. 16, lines 23-27).

Nowhere do Das et al. teach or suggest reinforcing fibers having an applied chemical treatment on the fibers from 5% to 30% by weight, as Applicants claim. Das et al. specifically teach "The aqueous chemical treating composition was added to the glass fibers during their formation at such a rate of forming the glass fibers….to result in strands having a dried residue of around 0.1 to 3 weight percent of the aqueous chemical treating composition." (col. 13, lines 12-17).

Applicants claim a significantly higher percentage of treatment on the fibers than either Dana et al. or Das et al. Because neither Dana et al. nor Das et al. teach or suggest all of Applicants' claim limitations and one would not be motivated to apply a significantly higher percent of treatment on fibers, as discussed above, a *prima facie* case of obviousness cannot be established.

Claims 2, 6, 9-10 and 12-15 ultimately depend from claim 1 and contain the limitations thereof. Accordingly, Applicants respectfully request that the 103(a) rejection of claims 1-2, 6, 9-10 and 12-15 be withdrawn.

Rejection of Claims 1, 4-5 under 35 U.S.C. 103(a)

Claims 1, 4-5 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Dana et al. (5,908,689) in view of Das et al. (4,637,956) and further in view of Eichhorn et al. (U.S. 4,596,736).

As argued above, neither Dana et al. nor Das et al. teach or suggest Applicants' claimed invention, as amended. In view of the arguments presented above, Applicants respectfully request that the 103(a) rejection of claims 1, 4-5 be withdrawn.

Conclusion

In view of the above, it is submitted that the claims are in condition for allowance. Reconsideration of the rejections is requested. Allowance of claims 1-2, 4-6, 9-10 and 12-15 at an early date is solicited.

The Examiner is invited to telephone the Applicants' undersigned agent at (740) 321-7213 if any unresolved matters remain.

If any questions should arise with respect to the above Remarks, or if the Examiner has any comments or suggestions to place the claims in better condition for allowance, it is requested that the Examiner contact Applicants' agent at the number listed below.

Applicant authorizes any fees required pertaining to this response be charged to Deposit Account No. 50-0568.

Respectfully submitted,

By: ______________________
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Date: August 13, 2004

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Interfaces and Interphases

Lawrence T. Drzal, Michigan State University

FIBER-MATRIX ADHESION is a variable to be optimized in order to get the best properties and performance in composite materials. The contemporary view of adhesion rests on an *interphase* model in which not only the actual chemical and physical interactions between fiber and matrix are considered, but also the structure and properties of both the fiber and the matrix in the region near the interface. While not a "phase" in the true sense of the word (that is, an identifiable volume with uniform properties), the term has come to be used to describe a region of finite dimensions where the local properties vary from those of the bulk phases. Although our understanding of this interphase is far from complete, the studies completed to date provide some insight into selection of surface treatments and finishes for certain classes of fiber and matrix constituents. An optimal design methodology starts with the specification of the fiber and matrix from a structural consideration. Once the constituents are selected, the focus is on the creation of a beneficial fiber-matrix interphase. This interphase region where the fiber and matrix interact has to be designed for both processing and performance. Although no quantitative models are available for interphase optimization, various thermodynamic and materials science principles coupled with a growing body of experimental data allow us to understand the interphase as well as to qualitatively design the interphase. The tools available for analysis and design include selection of surface treatments for surface structural and chemical modification; the use of surface finishes and/or sizes to ensure thorough wetting and protection of the fiber; creation of interphases with desirable stiffness, toughness, and failure modes; and quantitative and qualitative characterization tests for measuring fiber-matrix adhesion levels compatible with the structural environment and constituent materials.

Interface and Interphase

A composite material is the combination of any two or more constituents, one of which has superior mechanical properties but is in a difficult-to-use form (e.g., fiber, powder, etc.). This superior constituent is usually the reinforcement, while the other constituent (the matrix) serves as the medium in which the reinforcement is dispersed and serves to transmit external loads from reinforcing fiber to fiber. The resultant composite is a material whose properties are close to those of the reinforcement constituent, but in a form that can be easily fabricated into a structural component. Included in this definition of the reinforcing materials are particulate, fiber, flake, and sheet reinforcements. Matrices may be ceramic, metallic, polymeric, and cementitious.

Interface. Since their inception, composite materials behavior has been predicated on the use of structure-property relationships accounting for the fiber and matrix constituents. Factors such as constituent composition, physical morphology, and geometrical arrangement have been incorporated in models that can predict composite mechanical behavior. Since the 1980s, however, the realization that "acceptable" properties of the interface between reinforcement and matrix are necessary for coupling of the reinforcement to the matrix and behavior that agrees with the structure-property models, for example, rule-of-mixtures. An optimized interface is necessary for the composite to achieve maximum static and dynamic mechanical properties and environmental resistance. Indeed, interfacial adhesion between fiber and matrix is based on empirical methods for optimization in most commercial composites marketed today. In optimized commercial materials, the interface functions as an efficient transmitter of forces between fiber and matrix. As such, as long as the interface is intact, composite materials behavior can be adequately described by models that assume ideal adhesion between fiber and matrix and consider the interface to be a two-dimensional boundary.

Interphase. Fiber-matrix adhesion is viewed as a necessary criterion for achieving acceptable composite properties. The patent literature contains numerous chemical formulations, processes, and procedures designed to increase fiber-matrix adhesion levels so that acceptable composite mechanical properties could be achieved. As our understanding of the relationship of fiber-matrix adhesion to composite mechanical properties has increased (Ref 1), it has become apparent that adhesion not only is necessary, but also, if properly designed, can enhance the composite mechanical properties and performance. Although our quantitative understanding of the fiber-matrix interface and the mechanisms of adhesion is not completely developed at this time, it is possible to optimize the fiber-matrix interphase in much the same manner as composite design methodologies are optimized. The key to success in this endeavor is using the concept of a fiber-matrix interphase as a framework upon which to build this methodology. For the illustration of the concept of "interphase," comments will be directed to and examples will be selected from polymeric matrix composites.

Research since 1990 has expanded the concept of the fiber-matrix interface, which exists as a two-dimensional boundary, into that of a fiber-matrix *interphase* that exists in three dimensions (Ref 2). The complexity of this interphase can best be illustrated with the use of a schematic model, which allows the many different characteristics of this region to be enumerated, as shown in Fig. 1.

By definition, the interphase exists from some point in the fiber where the local properties begin to change from the fiber bulk properties, through the actual fiber-matrix interface, into the matrix where the local properties again equal the bulk properties. Within this region, various components of known and unknown effect on the interphase can be identified. For example, the fiber may have morphological variations near the fiber surface, which are not present in the bulk of the fiber. The surface area of the fiber can be much greater than its geometrical value, because of pores, pits, or cracks present on the surface. The atomic and molecular composition of the fiber surface can be quite different from the bulk of the fiber. Surface treatments can add surface chemical groups or remove the original surface, giving rise to a chemically and structurally different region. Exposure to air before composite processing can result in the adsorption of chemical species, which may alter or eliminate certain beneficial surface reactivity. These adsorbed materials may also desorb at the elevated temperatures seen in composite fabrication and be a source of volatiles, which, if not removed, can be the origin for voids that disrupt the interface. The thermodynamic surface energy of the fiber is a result of these factors. A necessary condition for acceptable interfacial interaction between the reinforcement and the matrix is determined by

contact with another hard surface can introduce critical-sized flaws that reduce strength. The 100 nm surface finish layer prevents actual contact between reinforcing entities. Finishes can be used with any reinforcement and have been developed primarily by the textile industry to aid in keeping fiber tows together during the textile steps that are sometimes required in composites manufacture. They find the widest use with carbon- and polymeric-reinforcing fibers. Another use for surface finishes is to protect the surface chemistry from environmental attack or contamination of the surface and consequent reduction in the surface free energy. Because the finish is an unpolymerized layer, exposure to the matrix or essentially the same composition during processing allows the finish to be solubilized and removed from the fiber surface.

From a processing viewpoint, finishes are very helpful in assisting and ensuring that the wetting and infiltration steps are complete. Well-designed surface finishes promote infiltration, disbursement, and wetting of individual reinforcements by their presence. Because the finishes are placed on the reinforcements from solution (both organic solvent and water-based), retention of solvent and volatilization during the early portion of the processing cycle is a potential problem. The high surface area of the fibers, their small size, and their large volume make the generation of voids a potential problem. If the composition of the finish is susceptible to chemical aging during long-term ambient storage, its solubility may be reduced to the point where it becomes confined to the fiber-matrix interface and is detrimental to both processing and adhesion.

Surface Sizings. In the composites industry, the term "sizing" has come to mean any surface coating applied to a reinforcement to protect it from damage during processing, aid in processing, or improve the mechanical properties of the composite. Surface sizings are similar physically to surface finishes, that is, they are applied to the fibers in thicknesses of approximately 0.1 μm, but differ in their chemical composition. They are almost always used with glass fibers and sometimes used with other reinforcements. Surface treatments are sometimes confused with sizings, especially in carbon-fiber reinforcement technology (Ref 7). The distinction between sizing and surface treatment is fairly clear in the case of carbon fibers, but is less clear in the case of boron fibers that are treated chemically to form a boron carbide or boron nitride coating (Ref 8). A useful definition is that a sizing is a deliberate coating of the reinforcement, which may incidentally react chemically with the surface; a surface treatment is a deliberate chemical modification of the reinforcement, which may incidentally result in the formation of a coating. Other terms used synonymously for sizing include finishing agent, which comes from the textile industry and refers to fiber coatings that render flexibility, drape, and special features, such as fire retardance, to fabrics. This term still finds use in fibrous composite nomenclature, especially for woven glass or carbon-fiber products. Sometimes sizing is referred to as a coupling agent when it is designed to enhance composite mechanical properties or durability.

Typical sizings solutions (Ref 9) contain a silane coupling agent or combinations of coupling agents, as well as other ingredients, such as film formers, antistatic agents, and lubricants. Sizings are applied to glass fibers from solution immediately at the point of glass manufacture. They are formulated to protect the glass-fiber surface from corrosive attack by water from the ambient environment. The silanes are hydrolyzed and react with glass-fiber surface hydroxyls to form very stable siloxane bonds. The remaining ingredients in the sizings systems are there to protect the glass surface from mechanical damage and to promote infiltration by the matrix. Titanate and zirconate chemistries are also used in addition to silane chemistries.

Sizings designed to protect the reinforcement during processing must coat the surface uniformly. For this reason, polymers that are widely used in the coating industry because of their good film-forming ability (Ref 10) are also used as sizing agents. Typical examples are starch and starch derivatives, the vinyl polymers, and the phenoxys. The choice is dictated by a number of considerations: compatibility with the matrix polymer, the level of protection required (for example, weaving is more severe on continuous fibers than prepregging of unidirectional tape), pliability or drape of the sized tow or cloth (for example, a stiff, "boardy" fabric is difficult to process), and cost. Sizings are usually applied at a level of 1.0 wt% or less, making it necessary to remove and dispose of large volumes of solvent. Environmental pollution and cost considerations mandate that the sizing be applied from aqueous media, which requires that it be soluble in water or able to be applied as a water-based emulsion.

Ideally, a sizing should be chemically compatible with the matrix polymer and should not adversely affect the mechanical properties of the interphase between reinforcement and matrix. If these requirements cannot be met, the sizing may be removed by washing or heating before processing the reinforcement into the final composite form. However, these manipulations usually either damage the fiber or leave residues that may prevent good bonding between reinforcement and matrix. Nevertheless these fugitive sizings are still used, especially for woven reinforcements.

There are a variety of film-forming polymers that are compatible with the more widely used polyester and epoxy-matrix resins. However, there are very few sizings that can be used with the newer high-temperature matrix polymers, such as the bismaleimides and polyimides, or with the tough thermoplastic matrices, such as polyphenylene sulfide or polyether etherketone. One approach to developing sizing for these newer matrix materials is to use the polymers themselves as the sizing. However, they usually do not have the wetting and spreading behavior necessary to form a uniform coating. Developing sizings for these new matrix polymers, especially for carbon-fiber-reinforced composites, is essential in order to realize their full potential.

Sizing systems are usually proprietary, and the manufacturer's recommendations must be followed, especially the storage conditions. Sizing systems are reactive, and the chemical reactions that can occur during long-term storage can make the sizing insoluble and/or lower in surface free energy, resulting in poor infiltration and wetting. Sizings are an essential factor in fibrous composites technology. They are critical in composites manufacturing and can have both negative and positive effects on composites properties. A sizing may adversely affect the mechanical properties of the composite. For example, a sizing that holds the filaments in a bundle so that the strand (tow) can be chopped for discontinuous fiber composites hinders later efforts to disperse the fibers during injection molding or extrusion.

As stated earlier, in commercial practice, the silanes are often applied with a film-forming polymer. Presumably, the coating polymer becomes entangled in the silane network along with the matrix polymer. The composition of this complex interphase is critical to understanding the moisture durability of composite materials. The possible interpenetration formation of silane and epoxy molecules is a subject of recent study (Ref 11).

Surface Modification Examples

Adhesion between fiber and matrix and its modification for composite structural applications must start with consideration of the stresses that the structural element will experience in its operational environment. In addition, the thermal and chemical (i.e, moisture) environments must be specified. This in turn dictates the fiber and matrix constituents to be used in the composite. The interphase will change depending on the matrix (e.g., thermoset or thermoplastic) as well as the reinforcing fiber (e.g., glass, carbon, or polymeric). Each constituent has different but related requirements for the interphase from both a processing and performance perspective.

Glass Fibers. For example, in glass fibers, the native fiber surface is mainly an inorganic oxide. This surface quickly adsorbs water that creates a hydroxylated surface. If exposure to moisture is continued, the adsorption of water corrodes the fiber surface, creating critical-sized flaws that reduce fiber strength. This corrosion process can vary in intensity, depending on the glass-fiber composition. In all cases, however, the glass surface must be protected from the chemical attack of water. Organofunctional silanes, titanates, and/or zirconates (Ref 12) are produced for this purpose and have been shown to be very effective in reducing or eliminating corrosive attack of the glass surface (Ref 6).

The silanes readily form three-dimensional polysiloxane networks through hydrolysis and condensation of the alkoxy groups. This poly-

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Industry Overview: Critical fiber sizing

By: Staff

Critical fiber sizing

To achieve desirable properties in composite components, adhesion between fiber and matrix must be optimized. Adhesion requires that sufficient saturation with resin (wetout) at the fiber-matrix interface. To ensure good adhesion, attention must be given to fiber surface preparation, such as the use of a surface finish or coupling agent, often termed sizing. Sizing, applied to glass and carbon filaments immediately after their formation, actually serves three purposes: As it enhances the fiber/matrix bond, it also eases processing and protects the fibers from breakage during processing. Although it accounts for only 0.25 to 6.0 percent of total fiber weight, sizing is a dynamic force in fiber reinforcement performance. Sizing chemistry distinguishes each manufacturer's product and can be optimized for manufacturing processes such as pultrusion, filament winding and weaving. For example, developments in sizing formulations have variously resulted in more cleanly chopped glass with reduced fuzz, glass that wets out more efficiently, and glass fibers that contain no chromium compounds.

Sizing is equally important for carbon fiber. Traditionally, carbon fiber was sized only for compatibility with epoxy resin. Today, fiber manufacturers are responding to demands from fabricators and OEMs to produce carbon fiber forms compatible with a broader range of resins and processes. For example, sizing is critical to dispersing chopped carbon in the sheet molding compound (SMC) used in some new automotive body panels, and fiber manufacturers have developed new sizings for resin infusion molding of carbon reinforcements with vinyl ester resin.

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Composite Basics

Material choices and properties you'll need to consider.

What we today call composites, or more specifically, fiber-reinforced plastics, were first produced about 50 years ago. While technically the term composite can apply to any combination of individual materials, we will focus on the design, manufacture and use of fibers, primarily glass, that have been impregnated with a plastic matrix resin.

Composites offer many advantages over traditional materials: chief among these are high strength, light weight, flexibility in design parts consolidation, high dielectric strength, dimensional stability, corrosion resistance and low tooling costs. While not quite a household name, composites have worked their way into a seemingly endless number of applications. They have virtually replaced other traditional materials in the recreational boating market. In the transportation industry, composite structural components enjoy popularity because of their tremendous strength-to-weight properties and impressive design flexibility. Due to their high strength and light weight, aerospace and high performance sporting goods utilize premium composite materials such as carbon fiber and epoxies. Because of their electrical insulating properties, composites are used widely in appliances, tools and other machinery. Additionally, corrosion-resistant composite tanks and pipes offer extended service life over metals.

DESIGN FLEXIBILITY

In arithmetic, adding one and one makes two. In fiber-reinforced plastic, adding fibers to a resin matrix creates one material whose properties cannot be predicted by summing the properties of its components. In fact, one of the main advantages of composites is the complementary nature of the components. For example, thin glass fibers are quite strong but they are also susceptible to damage. In comparison, certain plastics are relatively weak but extremely versatile and tough. The combination of these components can create a material that is more useful than either of the individual components. By carefully selecting the fiber, resin and manufacturing process, designers can tailor composites to meet final product requirements that could not be achieved using other materials.

While it is this combination of matrix, fiber and manufacturing process that gives composites their superior performance, it is essential to consider these elements separately.

Select the element you wish to review or scroll down to view the entire text

Types of Fiber		Forms of Reinforcement
Resins		Fillers

roving typically costs about $ per pound, depending on the quantity purchased, filament diameter and other factors. Corrosion-resistant roving sells for about 30 percent more than E-glass. At about $6 per pound, S-2 glass roving is much more expensive than either E-glass or corrosion-resistant glass. Product designers must weigh the benefits of advanced glass fibers against their higher cost.

FIBER MANUFACTURING

Fiber properties that determine how a final product will perform are based, in part, on the fiber manufacturing process. Processing complexity and material costs also determine glass reinforcement prices. During fiber production, bulk materials transform into web-like fans of delicate (and highly abrasive) glass filaments ranging in diameter from 315 to 24 micrometers. Silica sand is the primary ingredient, accounting for more than 50 percent of the raw materials. Additional materials used in producing E-glass include limestone, fluorspar, boric acid and clay. By varying raw materials and processing parameters, other glass types can be produced.

After the raw materials are mixed thoroughly, they enter a furnace operating at 2500° to 3000° F. Fired by natural gas and/or electricity the furnace melts the raw materials, which then flow into one or more bushings. These bushings contain hundred (and sometimes thousands) of small orifices through which the molten glass flows. The molten glass filaments immediately enter a quench area where water and/or air quickly cool the filaments to below the glass transition temperature.

In a typical glass fiber forming process, the filaments are then pulled over a roller, which coats them with sizing. Traveling at high speed, each filament fan is pulled into a single strand and wound onto a tube. A strand typically contains hundreds of filaments and may contain more than 1000 filaments. After the spindle on the winder becomes full, the filament cake is transported to an oven where the sizing dries and cures. Fiber strands from the filament cake are then used to produce rovings and chopped fiberglass. Multiple filament cakes are placed into creels then grouped together to form rovings.

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SIZING IS CRITICAL

Sizing is applied to the filaments immediately after their formation to ease processing, protect the fibers and create better bonding between the fiber and the resin matrix. On a weight basis, 0.25 percent to 6 percent sizing is applied to the fiber. Without sizing, glass fiber essentially could not be processed, typically some form of lubricating oil is present in the sizing to reduce friction and abrasion that occurs during manufacturing. Traveling at speeds of 50 miles per hour or more, the filaments abrade processing machinery. This abrasion leads to loss of tensile strength due to filament surface damage.

Sizing also includes chemical components designed to protect the fibers from moisture and